3d-4f Metal Coordination Polymers

A Nanotubular 3D Coordination Polymer Based on a 3d–4f Heterometallic Assembly**

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Interest in porous metal-coordination polymers that are constructed by self-assembly processes has mushroomed recently,[1] because of their use in, for example, redox catalysis, cathodic electrolysis, ion exchange, adsorption, separation, sensors, and molecular recognition.[2–5] However, much of the work has so far focused on coordination polymers containing transition metals,[2,6] while rare-earth metal compounds have received much less attention.[7] To date, no systematic investigation of zeolite-type structures containing metal atoms from the lanthanide series along with transition-metal atoms has been documented. Furthermore, the pores or channels reported were mainly formed through either hydrogen bonding,[2b] or π–π packing,[1b] and only in a few cases were they formed through metal–ligand bonding alone.[1c7f] On the other hand, the construction of mesoporous metal-–organic polymers suffers from difficulties in the control of the polymer dimensionality. Although ligands can be designed to create a large hole, the resulting coordination polymers are often plagued by lattice interpenetration,[8] or framework breakdown on removal of a guest molecule.[9] In addition, the variable and versatile coordination behavior of 4f-metal ions limits their selective introduction into highly ordered structures.

Herein we report the syntheses and structures of three coordination polymers formed through hydrothermal synthesis: $[\{[\mathrm{Ln(dipic)_3Mn_{1.5}(H_2O)_3}]\cdot n\,\mathrm{H_2O}\}_\infty]$, $\mathrm{H_2dipic}$ = pyridine-2,6-dicarboxylic acid; Ln = Pr, $n=2$ (**1**); Ln = Gd, $n=3.5$ (**2**); Ln = Er, $n=3$ (**3**). These compounds have the relatively large nanometer-sized tubes associated with self-assembly processes directed by metal–ligand coordination only, and the framework remains intact on removing water molecules trapped in the nanotube.

The three compounds are stable in air and are insoluble in common solvents. Single-crystal X-ray diffraction analyses were performed on selected crystal of these compounds. The crystal structures of the polymers are isomorphous, comprising a 3D framework containing nine-coordinate lanthanide-metal centers and six-coordinate transition-metal centers, which results in a nanotubelike structure (Figure 1). All three polymers crystallized in the hexagonal crystal system, space group *P6/mcc*. The crystal structure is built up of two distinct types of building blocks, $\mathrm{Ln(dipic)_3}$ and $\mathrm{MnO_4(H_2O)_2}$ (Figure 2). The Ln atom is located at the intersection of a threefold and a twofold axis and is coordinated by three tridentate (ONO) dipic anions; for which each carboxy group coordinates through one oxygen atom. Three N atoms and six O atoms complete the coordination sphere of the $\mathrm{Ln^{3+}}$ center, which conforms most closely to a tricapped trigonal prism. The coordination geometry around $\mathrm{Mn^{2+}}$ center is a slightly distorted octahedron, the equatorial plane of which comprises four O atoms from the carboxy groups of the dipic molecules that are chelated to four neighboring $\mathrm{Ln^{3+}}$ centers; two water molecules occupy the remaining apical coordinate sites. Each Mn atom is located at the intersection of a mirror plane and a twofold axis, namely the crystallographic 6*g* position of the *P6/mcc* space group, and its site symmetry is *2/m*. There are three crystallographically independent dipic molecules in the structure, each has the same coordination mode, that is, chelated to one Ln atom, and linked to two Mn atoms. One

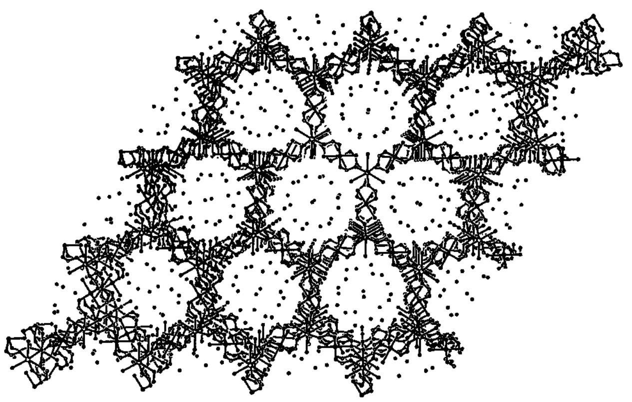

Figure 1. Projection of the 3D framework down the *c* axis in **1**; the C atoms of the pyridine rings and H atoms are omitted for clarity.

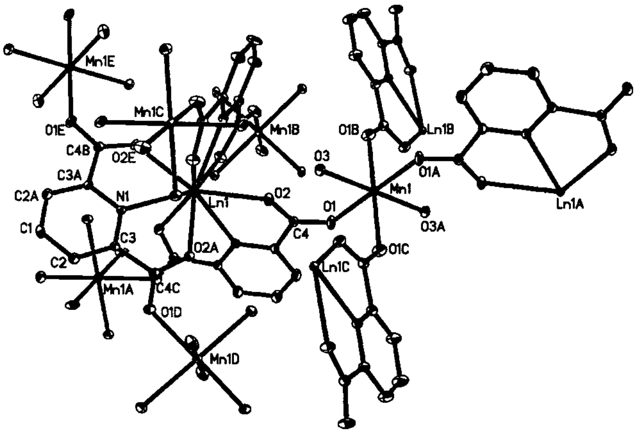

Figure 2. Diagram showing the two building units with atom labels of the Mn–Ln series; H atoms are omitted for clarity. Symmetry operations: A: 1+*y*, *x*, 0.5−*z*; B: *x*−*y*, −*y*, 0.5−*z*; C: 1−*x*+*y*, 1−*x*, *z*; D: 1−*y*, *x*−*y*, *z*; E: 1−*x*, 1−*x*+*y*, 0.5−*z*.

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oxygen atom from any carboxy group bonds to an Ln^{3+} center and the other oxygen atom bonds to an Mn^{2+} center; thus each Ln^{3+} center has six Mn^{2+} ions as the nearest metal center, while the Mn^{2+} center has four Ln^{3+} ions in its vicinity (Figure 2), as is consistent with the Mn:Ln molar ratio. Carboxy bridges exist between adjacent Ln and Mn atoms, and more importantly, each carboxy group also bridges each Mn–OCO–Ln unit, which creates a highly ordered 3D structure with tubular channels with a diameter of about 17.9 Å for **1** (defined by the separation between Pr1 and Pr1D, Figure 3 a) along the [001] direction, as shown in Figure 1. Notably, many guest water molecules were trapped in the parallel tubes. A cross section of a nanotube (for Nn = Pr(**1**); Figure 3 a) shows a 48-membered ring (48MR) comprising 6 Ln, 6 Mn, 12 C, and 24 O atoms, of which, the Ln and Mn atoms are arrayed alternately and connected by O–C–O bridges, thus leading to an overall C_6 symmetry. Six Ln atoms and six Mn atoms are rigidly coplanar and the distance between both planes is about 3.92 Å for **1** . The wall of the nanotube is made up of 16MRs (2 Ln, 2 Mn, 4 C, and 8 O atoms in each ring; ca. 5.91 × 5.91 Å for **1**). Compounds containing 18MRs,[10] 20MRs,[11] 24MRs,[12] and 30MRs[13] are well documented, however, to the best of our knowledge, 48MRs have not been previously reported. The Ln–O distance decreases with increasing lanthanide atomic number (Pr–O 2.501, Gd–O 2.442, and Er–O 2.411 Å) and the same trend is seen for Ln–N bond lengths and is interpreted as a result of the lanthanide contraction.

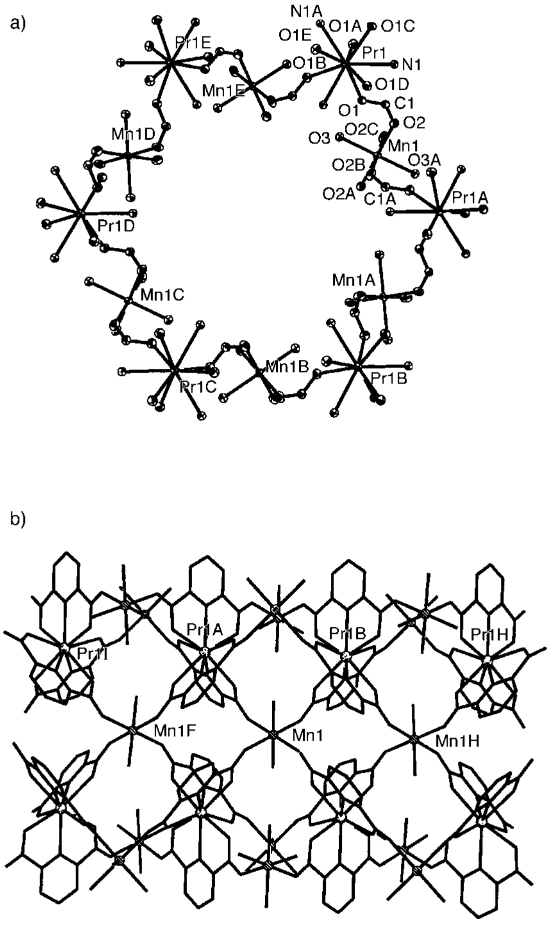

Figure 3. a) The cross section of the nanotube for **1**, which shows 48MRs and C_6 symmetry; the C atoms of the pyridine rings and H atoms are omitted for clarity. b) The 16MR structure of the tubular wall in **1**; H atoms are omitted for clarity.

Thermal gravimetric analysis (TGA) reveals that these complexes can adsorb water molecules as a consequence of the large pores present. TGA was performed on crystalline samples of these compounds in the range of 14 to 620 °C. The weight loss of 9.43 % for **1** and 8.81 % for **3**, between 40 and 140 °C corresponds to the loss of all uncoordinated and adsorbed water molecules (calcd 8.52 % for $\mathbf{1}\cdot 2H_2O$ and 8.27 % for $\mathbf{3}\cdot H_2O$). This is indicative of the adsorption of two water molecules per $PrMn_{1.5}$ unit of **1** and just one water molecule per $ErMn_{1.5}$ unit of **3**, and is consistent with the elemental analyses (EA) of $\mathbf{1}\cdot 2H_2O$ and $\mathbf{3}\cdot H_2O$. For comparison, TGA and EA experiments for **2** were carried out after **2** had been dried, and the results show no adsorption of water into the pores; the weight loss of 7.1 % below 140 °C (calcd 7.4 %) corresponds to the loss of 3.5 uncoordinated water molecules per Gd/$Mn_{1.5}$ unit of **2**. Taking **1** as an example, we explored whether the framework would break down on removal of guest water molecules (uncoordinated and adsorbed water molecules). Water molecules were removed by heating **1** at 120 °C for 12 h. Powder X-ray diffraction patterns of hydrated and dehydrated samples of **1** are nearly identical, which supports the notion that the crystal lattice remains intact after the guest water molecules have been removed. TGA showed that samples of **1**–**3** lost coordinated water molecules between 140 and 280 °C, but did not decompose until 340 °C.

Magnetic measurements on the three coordination polymers show interesting behavior in a 10 kOe magnetic field. The plots of $\chi_M T$ versus temperature for polymers **1**–**3** are given in Figure 4. For **1**, $\chi_M T$ steadily decreases with decreasing temperature from 300 to 15.6 K, and dramatically drops to 5.14 $cm^3 K mol^{-1}$ at 2 K. For **3**, the plot of $\chi_M T$ versus temperature is similar in shape to that of **1**. The observed $\chi_M T$ values for **1** and **3** were 8.49 and 17.58 $cm^3 K mol^{-1}$ at 297 K, respectively, which are close to the theoretical values of 8.16 and 18.04 $cm^3 K mol^{-1}$, respectively, as expected for 1.5

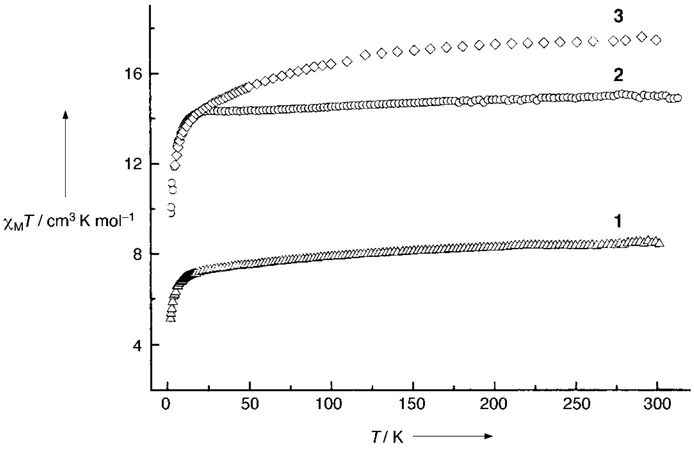

Figure 4. Plots of $\chi_M T$ versus T for **1** (△), **2** (○), and **3** (◇).

Mn^{II} ions and one Pr^{III} (**1**) or Er^{III} (**3**) ion for the corresponding ground states $^3H_4$ ($g = 4/5$) and $^4I_{15/2}$ ($g = 6/5$), respectively. The coupling interactions between Pr and Mn, and between Er and Mn, are not explicitly characterized because of the strong spin–orbit coupling of the lanthanide atoms.[14] Attempts to explore in detail the magnetic interaction between Ln^{III} and Mn^{II} ions by synthesizing isomorphic coordination polymers to **1** and **3** containing diamagnetic transition metal ions have thus far failed.

The very slow decrease in the value of $\chi_M T$ for **2** with decreasing temperature from 14.95 $cm^3 K mol^{-1}$ at 313 K to 14.19 $cm^3 K mol^{-1}$ at 17.4 K, might be attributed to antiferromagnetic coupling between the Gd^{III} and Mn^{II} ions. Compared with the ferromagnetic coupling of the Gd^{III} and Cu^{II} ions,[14,15] the Mn^{II} ion with a $3d^5$ electronic configuration is very stable in energy, and unpaired electrons around Mn^{II} are very difficult to transfer to the 5d or 6s orbitals of the Gd^{III} ion. On the other hand, the nonzero overlapped integration between the Gd^{III} and Mn^{II} ions would result in an antiferromagnetic interaction between Gd^{III} and Mn^{II} ions within **2**.

In summary, we have synthesized three novel lanthanide–transitional-metal coordination polymers by hydrothermal reactions. They are the first 3d–4f zeolite-type structures containing nanotubes comprising 48MRs and have a previously unknown framework topology with the space group *P6/mcc*. The walls of the nanotubes include 16MR windows resulting in an unprecedented 3D 3d–4f heterometallic framework. Remarkably, the framework remains intact on removal of the guest water molecules. These results provide an opening into a promising new field of 3d–4f mixed-metal zeolite-type materials.

Experimental Section

Synthesis of **1**–**3**: A mixture of H_2dipic (0.8 mmol, 0.134 g), $Ln(ClO_4)_3 \cdot 6H_2O$ (Pr 0.109 g; Gd 0.113 g; Er 0.115 g), $MnCO_3$ (0.3 mmol, 0.034 g), and H_2O (10 mL) in the molar ratio of 4:1:1.5:2778 were put in a 20-mL acid digestion bomb and heated at 185 °C for three days. The products were collected after washing with H_2O (2 × 6 mL) and diethyl ether (2 × 6 mL).

Elemental analysis (%) calcd for $\mathbf{1}\cdot 2H_2O$: C 29.83, H 2.72, N 4.97; found: C 29.66, H 2.93, N 4.79. Crystal data of **1**: $[\{[Pr(dipic)_3Mn_{1.5}(H_2O)_3]\cdot 2H_2O\}_\infty]$, $M_r = 808.71$, hexgonal, *P6/mcc*, $a = b = 15.512(2)$, $c = 15.645(3)$ Å, $\gamma = 120°$, $V = 3260.2(9)$ Å^3, $Z = 4$, $\rho = 1.648$ g cm^{-3}, $2\theta_{max} = 50.06$ ($-18 \le h \le 14$, $-17 \le k \le 18$, $-18 \le l \le 14$), $T = 293(2)$ K, 12182 measured reflections. $R1 = 0.0305$ for 626 reflections ($I > 2\sigma(I)$), $wR2 = 0.0723$ for 998 independent reflections (all data) and 76 parameters. $GOF = 1.032$.

Elemental analysis (%) calcd for $\mathbf{2}\cdot 3.5H_2O$: C 29.58, H 2.58, N 4.93; found: C 29.37, H 2.90, N 5.11. Crystal data of **2**: $[\{[Gd(dipic)_3Mn_{1.5}(H_2O)_3]\cdot 3.5H_2O\}_\infty]$, $M_r = 852.03$, hexgonal, *P6/mcc*, $a = b = 15.307(3)$, $c = 15.695(4)$ Å, $\gamma = 120°$, $V = 3260.2(9)$ Å^3, $Z = 4$, $\rho = 1.664$ g cm^{-3}, $2\theta_{max} = 50.68$ ($-18 \le h \le 14$, $-17 \le k \le 18$, $-18 \le l \le 14$), $T = 293(2)$ K, 12182 measured reflections. $R1 = 0.0198$ for 655 reflections ($I > 2\sigma(I)$), $wR2 = 0.0475$ for 978 independent reflections (all data) and 76 parameters. $GOF = 0.995$.

Elemental analysis (%) calcd for $\mathbf{3}\cdot H_2O$: C 28.93, H 2.64, N 4.82; found: C 29.24, H 2.41, N 4.95. Crystal data of **3**: $[\{[Er(dipic)_3Mn_{1.5}(H_2O)_3]\cdot 3H_2O\}_\infty]$, $M_r = 853.08$, hexgonal, *P6/mcc*, $a = b = 15.229(2)$, $c = 15.852(5)$ Å, $\gamma = 120°$, $V = 3183.6(11)$ Å^3, $Z = 4$, $\rho = 1.780$ g cm^{-3}, $2\theta_{max} = 47.60$ ($-18 \le h \le 13$, $-18 \le k \le 17$, $-15 \le l \le 18$), $T = 273(2)$ K, 11457 measured reflections. $R1 = 0.0216$ for 625 reflections ($I > 2\sigma(I)$), $wR2 = 0.0523$ for 937 independent reflections (all data) and 74 parameters. $GOF = 1.028$.

CCDC-191516–191518 (**1**–**3**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or deposit@ccdc.cam.ac.uk).

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